Макрогетероциклы
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DOI: 10.6060/mhc140923k

Interaction of Dioxygen with Nitrosyl Complexes of *meso*–Mono–4(3)–pyridyltriphenylporphyrinatocobalt(II) in Sublimed Layers

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Dedicated to Corresponding member of Russian Academy of Sciences Prof. Oscar I. Koifman
on the occasion of his 70th birthday

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Sublimed layers of 5-(pyridin-4-yl)-10,15,20-triphenylporphyrinato)cobalt(II) and 5-(pyridin-3-yl)-10,15,20-triphenylporphyrinato)cobalt(II) ({Co(M4PyTPP)} (**I**) *and {Co(M3PyTPP)}* (**II**)*, respectively) form coordination oligomers upon standing. Interaction of NO(^{15}NO) gas with these systems results in the formation of penta- and hexacoordinated nitrosyl complexes, the sixth coordination site of which is occupied by pyridyl group of adjacent molecule in the layer. The FTIR spectral data demonstrate that the long-term exposure of these systems under O_2 results in oxidation of the nitrosyl complexes with formation of hexacoordinated nitrato complexes and the reaction proceeds predominantly with hexacoordinated nitrosyls. Mechanism of oxidation more likely includes the dissociation of NO from the hexacoordinated complex followed by O_2 trapping of resulting (-4(3)Py)Co(M4(3)PyTPP) to give (- 4(3)Py)Co(M4(3)PyTPP)(O_2), which then reacts rapidly with NO by the nitric oxide dioxygenation reaction.*

Keywords: *meso*-Substituted porphyrins, cobalt(II) complexes, coordination oligomers, nitrosyl complexes, FTIR spectra, oxidation by dioxygen, nitrato complexes.

Взаимодействие молекулярного кислорода с нитрозильными комплексами *мезо*–моно–4(3)–пиридил–трифенилпорфиринатов кобальта(II) в сублимированных слоях

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Посвящается Член-корреспонденту РАН Оскару Иосифовичу Койфману
по случаю его 70-летнего юбилея

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5-(Пиридин-4-ил),10,15,20-трифенилпорфиринато)кобальт(II) и 5-(пиридин-3-ил)-10,15,20-трифенилпорфиринато)кобальт(II), {Co(M4PyTPP)} (**I**) *и {Co(M3PyTPP)}* (**II**)*, формируют в сублимированных слоях координационные олигомеры. Такие системы при взаимодействии с NO (^{15}NO) образуют пента- и гексакоординационные* *нитрозильные комплексы. В последних в транс-положении к нитрозильному лиганду находится пиридильная группа соседней молекулы в слое. В работе приводятся ИК-спектральные доказательства того, что в атмосфере O_2 нитрозильные комплексы медленно окисляются с образованием гексакоординационных нитратных комплексов, причем в реакции задействованы преимущественно гексакоординационные нитрозильные комплексы.*

Ключевые слова: *мезо*-Замещенные порфирины, комплексы кобальта(II), сублимированные слои, ИК-спектры, нитрозильные комплексы, окисление молекулярным кислородом, нитратные комплексы.

Introduction

Thin layers of metal complexes of *meso*-tetraarylporphyrins obtained by sublimation onto the liquid nitrogen cooled surface, are amorphous and microporous. They provide unimpeded diffusion of ligands into the bulk of the layer, and the resultant adducts can be analyzed using spectral techniques without the interfering effect of the solvent and within a wide range of temperatures.[1] However, during storage at ambient conditions they lose this ability due to close packing of the molecules in the layer and dramatically decreased cross section of the pores that prevents the diffusion of potential ligands in to the bulk of the layer.

In contrast to metal complexes of *meso*-tetraarylporphyrins, sublimed layers of *meso*-pyridyl substituted derivatives with metal ion capable of axial coordination retain a microporous structure and the ability of reversible coordination of various ligands during storage.[2,3] This is due to the formation of zigzag type oligomeric structures by coordinating pyridyl group of one molecule with the metal ion of the adjacent molecule in the layer. For complexes with metals prone to octahedral coordination, such supramolecular organization leads to the formation of a penta- or hexacoordinated complexes.[2-5]

Nitrosyl complexes of metalloporphyrins are of considerable interest in biology and in medicine as potential sources of NO.[6] It has been previously shown,[4] that the reaction of NO with sublimed layers of **I** and **II** leads to the formation of two types of nitrosyl complexes: pentacoordinated – with molecules at the end of the oligomers and those not involved in the oligomeric structures; and hexacoordinated – with the sixth coordination site occupied by the pyridyl group of adjacent molecule in the layer. In this paper, the behavior of these systems is investigated when exposed to oxygen atmosphere and it is found that these are slowly oxidized forming hexacoordinated nitrato complexes.

Experimental

Co(M4PyTPP) (**I**) and Co(M3PyTPP) (**II**) were obtained using the corresponding metal-free porphyrins H_2M4PyTPP и H_2M3PyTPP, synthesized according to [7]. Their NMR and electronic absorption spectra were in good agreement with available literature. The Co-porphyrins were placed in the Knudsen cell and heated up to ~ 450 K under high vacuum to remove the solvated molecules. Then the cryostat was filled with liquid nitrogen and the temperature of the Knudsen cell was raised up to ~560 K, where **I** and **II** were sublimed onto a KBr substrate. In order to obtain layers with thicknesses suitable for infrared measurements, the deposition was performed for 1.5-2 hours. Nitric oxide, prepared by the procedure described in [8], was purified by passing it through a KOH tablet and trap cooled with acetone-dry ice bath in order to remove heavier oxides of nitrogen and trace amounts of moisture. The purity of the NO was controlled with infrared measurements of the condensate, obtained by its slow deposition on a cooled substrate of an optical cryostat (80 K). IR spectra did not reveal any presence of N_2O, NO_2, N_2O_3 or H_2O bands, thereby indicating their absence. ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes of the Republic of Georgia and purified by the same method. Molecular oxygen was stored in cylinders with P_2O_5 for the removal of the trace amounts of moisture.

The layers of **I** and **II** obtained via sublimation onto a low temperature substrate were heated up to room temperature and kept in vacuum overnight. On the next day small amounts of NO controlled by a mercury manometer were introduced into cryostat at low substrate temperatures. IR spectral control during the substrate temperature variation allowed the monitoring of the nitrosyl complex formation and its maximum obtainment. Long-term pumping of the cryostat was performed at elevated temperatures in order to remove the non-reacted NO. At such temperatures nitrosyl complexes were still not decomposed. Thereafter, various portions of oxygen were introduced into cryostat and the processes occurring in the layer were monitored by means of IR spectroscopy.

IR spectra were taken with "Nexus" Fourier transform spectrometer, the electronic absorption spectra with "Specord M-40" spectrophotometer and the NMR spectra with "Varian Mercury" spectrometer.

Results and Discussion

As mentioned in the Experimental part, layers of **I** and **II** obtained by sublimation on the low-temperature substrate, were kept under vacuum overnight. This procedure contributed to the growth of oligomeric structures in the layers. This process was easy to monitor for layers **I** by studying the behavior of a band at about 1600 cm^{-1}. The single medium intensity band of Co(TPP) in this spectral range representing the C=C stretching of the phenyl groups in **I** gains intensity and becomes complex due to mixing with the C=N stretching of pyridyl group (Figure 1). It can be seen from the spectra that this band exhibits well-defined changes upon annealing of the layer. The high frequency shoulder in low temperature sublimate gains intensity after annealing of the layer and, as a result, the peak's maximum shifts to higher wavenumbers by 7 cm^{-1}. This is evidence for an increasing fraction of coordinated pyridyl groups because it is known[9] that coordination of pyridine with metal ions leads to a high frequency shift of this vibration.

This band intensity is considerably lower in the spectra of **II**, the contribution of the pyridyl ring vibrations in this band is much smaller, and thus it cannot be used for monitoring purposes of the oligomerization processes in the layer. However, such information can be obtained indirectly from the ratio of the intensities of stretching vibrations of the

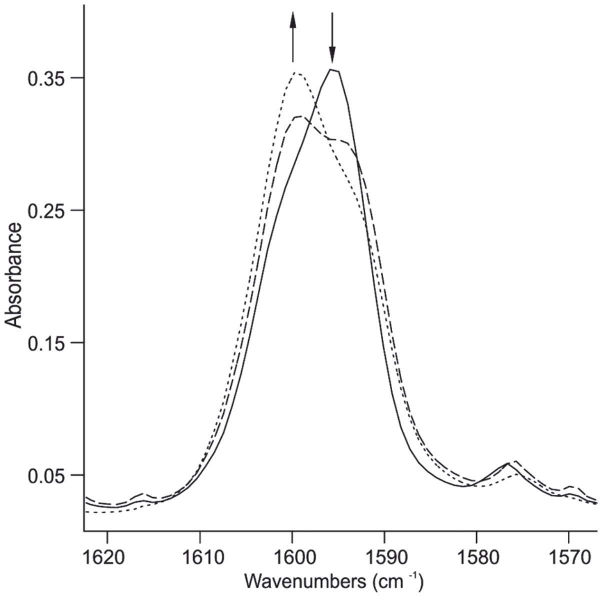


Figure 1. IR spectra of **I** at around 1600 cm^{-1} after deposition on the low-temperature substrate (solid line, T = 80 K), heating to room temperature (dashed line) and after keeping in vacuum overnight (dotted line).

simplest diatomic molecules in the penta and hexacoordinate complexes resulting from their interaction with layers **II**.

The initial curve in Figure 2 is an IR spectrum of sublimed layer of **II** after introduction of 6 torr NO into the system at low temperatures, subjection to 180-220-180 K temperature cycle and evacuation of the excess NO. Spectrum of **II** does not contain absorption bands around 1650 cm^{-1}. The intense band with a maximum at 1656 cm^{-1} in the spectrum represents a ν(NO) of the hexacoordinated nitrosyl complex with the pyridyl group of the adjacent molecule in its trans position. There is also a noticeably high frequency shoulder peaking at 1680 cm^{-1} in the spectrum which belongs to the ν(NO) band in the pentacoordinate complex. Nitrosyl complexes of Co-porphyrins with *trans* electron donor ligands were spectrally characterized at low temperatures. It is undeniable that the ν(NO) band undergoes low-frequency shift when compared to pentacoordinate complexes.[10,11] It is possible to state with confidence that the molecules in layer **II** are largely oligomerized, based on the intensities ratio of the ν(NO) bands of the penta and hexacoordinate nitrosyl complexes in the initial spectrum (Figure 2).

Introduction of ~10 Torr of O_2 into cryostat has practically no effect on the IR spectrum recorded immediately after the oxygen supply. However, the exposure of oxygen, extended overnight, leads to a growth of new bands in the spectrum (intermediate spectrum), indicating that oxidation processes are taking place in the layer. In particular, there is growth of bands with correlating intensities at 1490, 1270 and 970 cm^{-1}. The intensities of these get higher with the layer being kept in the oxygen environment (final spectrum). In the meanwhile, the nitrosyl band of the hexacoordinate complex completely disappears and only a band at 1681 cm^{-1} is left in the spectrum. This band is attributed to a mononitrosyl complex Co(M3PyTPP)(NO) – the analog to a well known nitrosyl complex Co(TPP)(NO), the first structurally characterized nitrosyl complex of the metalloporphyrin.[12]

Increased oxygen pressure significantly speeds up the oxidation of nitrosyl complexes and increases the proportion of the oxidized product, however, the process is still slow (see Figure 3). New bands, rising in the IR spectra have their isotopic counterparts in the experiments using ^{15}NO (Figure 4). These results show that the oxidation affects precisely the nitrosyl fragments of the systems under investigation. The remaining bands of the porphyrin do not undergo significant changes thus indicating that the oxidation processes do not affect the porphyrin ring.

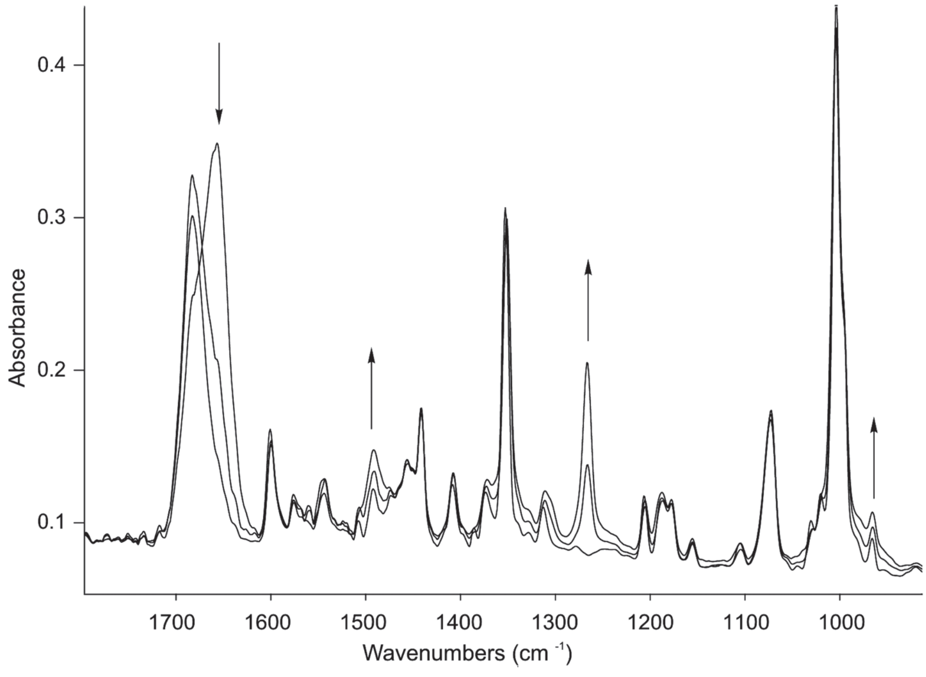


Figure 2. IR spectra of **II** + NO (initial spectrum) after overnight (intermediate spectrum) and 5-day (final spectrum) exposure to 10 Torr O_2 atmosphere.

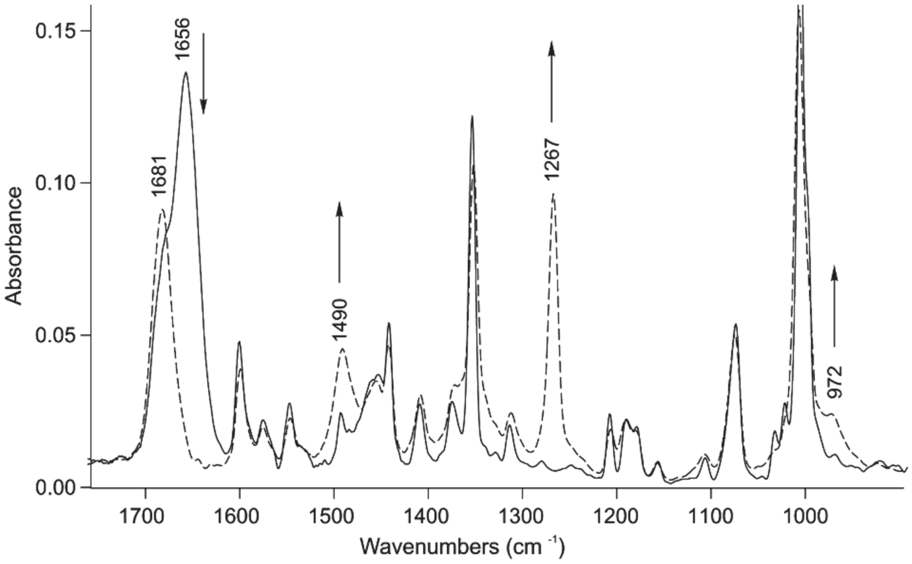


Figure 3. IR spectrum of system **II** + NO at 200 K (solid line) after exposure to O_2 atmosphere (P = 85 torr) at room temperature for 3 days (dashed line).

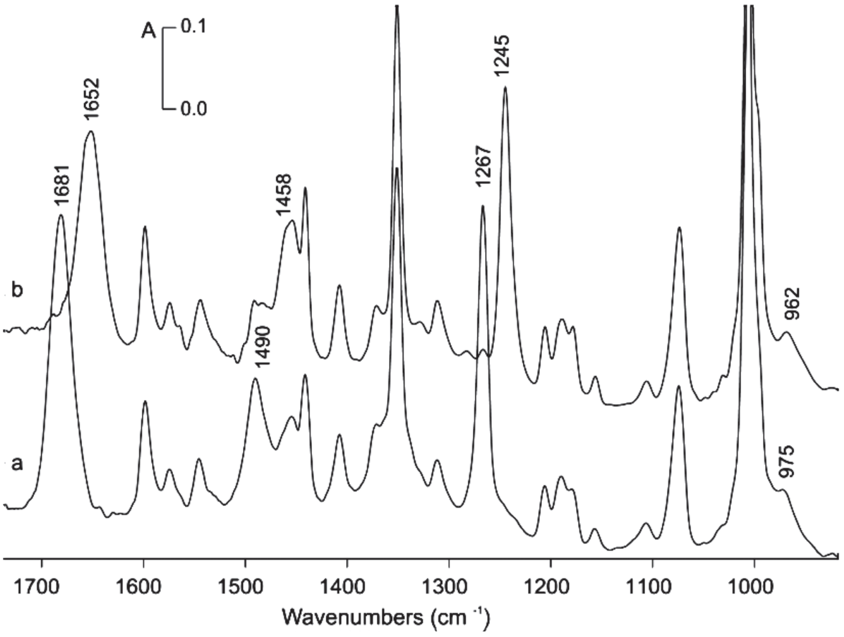


Figure 4. IR spectra of the sublimed layers **II** + NO (a) and **II** + ^{15}NO (b), exposed to oxygen atmosphere (P = 85 torr) for 3 days.

Sublimed layers of **I** behave similarly (Figure 5). However, it is noticeable from the ratio of nitrosyl and nitrato band intensities in the IR-spectrum that in similar experimental conditions the oxidation of **I** is at a lower level than that of **II (**Figure 5, solid line**).**

It is also possible to notice, that the relative quantities of hexacoordinate nitrosyl complexes in the sublimed layers of **I** are less than those in **II** (dashed line in Figure 5). This is a reason to assume that mainly hexacoordinate nitrosyl complexes are responsible for the oxidation processes in layers containing nitrosyl complexes of **I** and **II.**

From the values of frequencies, isotopic shifts and relative intensities the abovementioned bands are very close to those observed in hexacoordinate nitrato complexes of Fe- and Co(TPP) (Table 1). This is a very strong argument for their referral to the same structures.

Until recently, the hexacoordinate nitrato complexes of Fe- and Co-porphyrins were not known. In structurally characterized nitrate complexes of Fe(TPP)(NO_3)[13] and Co(OEP*)(NO_3)[14] (OEP* – modified octaethylporphyrinato ligand), in which nitrate is the only axial ligand, a bidentate coordination of a nitrato-group is realized with a significant displacement of a metal ion from the mean porphyrin plane.[15] This, in turn, creates a significant steric hindrance for the coordination of ligands in *trans* position. The three IR active stretching modes expected for this structure would be a high frequency ν(N=O) disposed around 1530 cm^{-1} for the uncoordinated oxygen and two (symmetric and asymmetric) modes for the coordinated

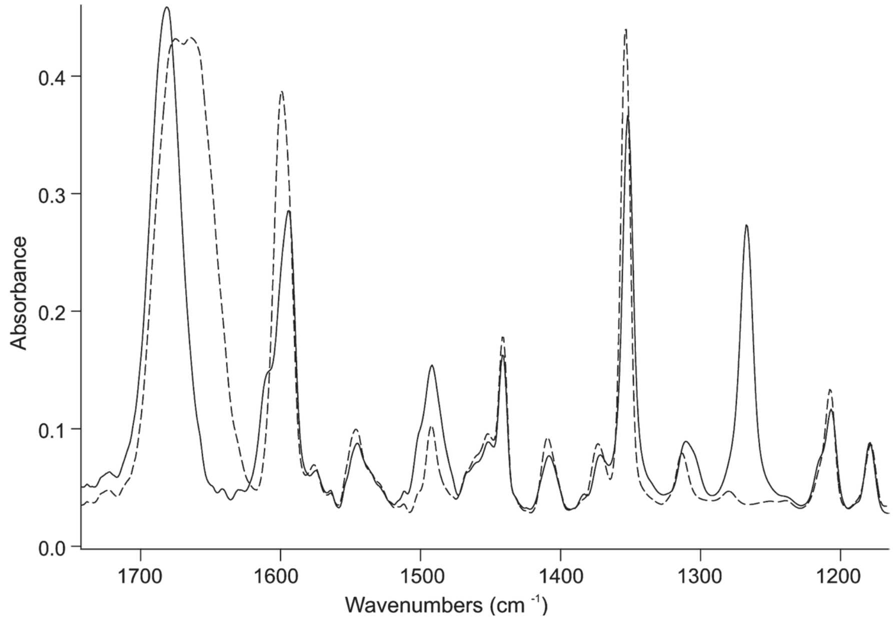


Figure 5. IR spectrum of sublimed layer **I** after introduction of 6 Torr NO into cryostat at 180 K, slow heating of the layer up to 220 K and evacuation of the excess NO (dashed line), and after exposure of the layer to O_2 atmosphere (90 Torr) for 3 days (solid line).

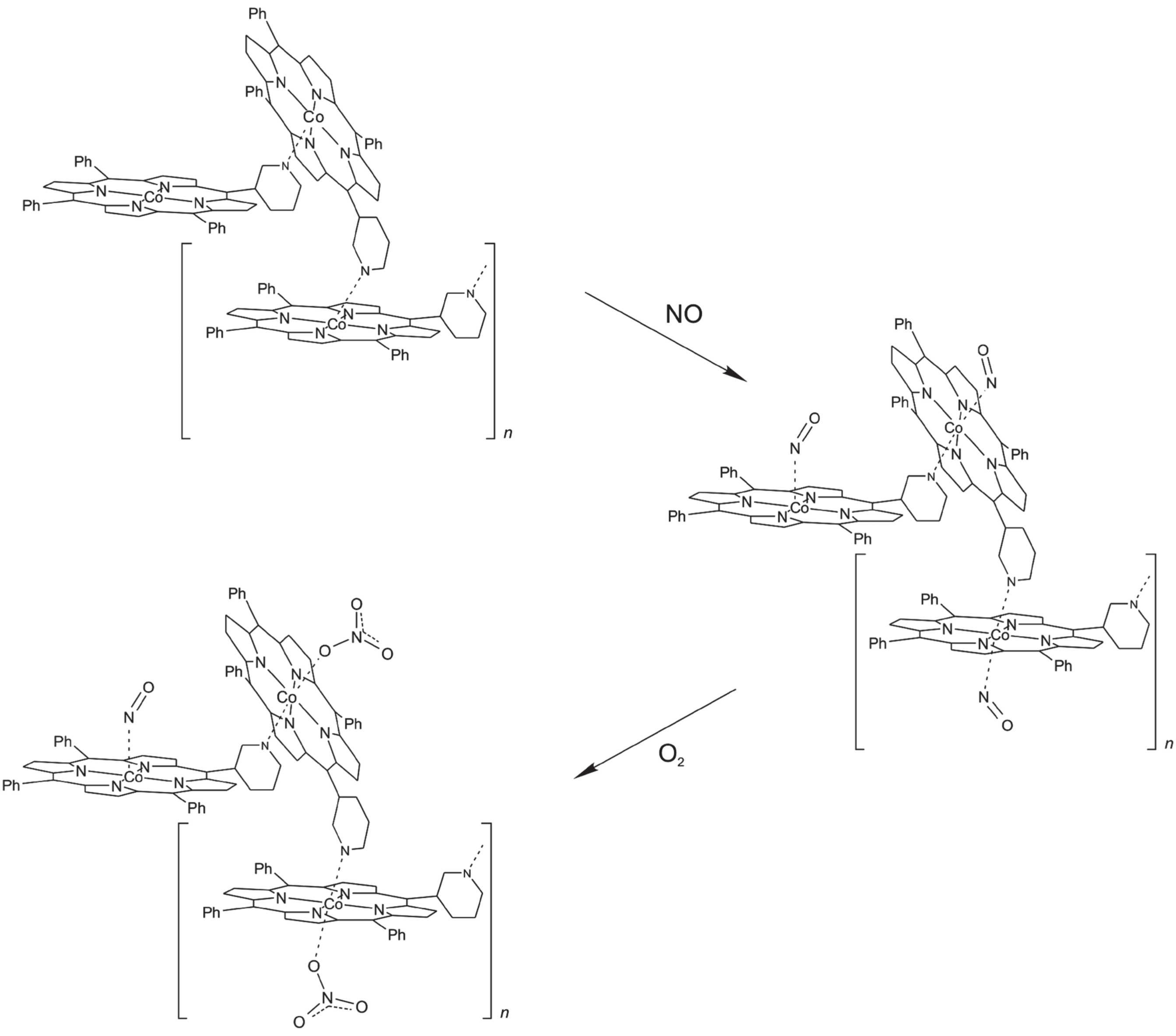
NO$_2$ fragment disposed in the vicinity 1260 and 990 cm^{-1}. The intensities of high frequency bands are close to each other while the band near 990 cm^{-1} is much weaker. Although formation of a hexacoordinate nitrate complex (Py)Co(TPP)(NO$_3$) in the disproportionation reaction 2(Py)Co(TPP)(NO$_2$) = (Py)Co(TPP)(NO) + (Py)Co(TPP)(NO$_3$) has been proposed on the basis of the IR bands at 1530, 1265 and 990 cm^{-1}[16] we believe that the mentioned compound is more likely to be a nitrato complex Co(TPP)(η^2-O$_2$NO) with the bidentate mode of coordination, as similar frequencies were observed in the spectrum of Fe(TPP)(η^2-O$_2$NO).[17]

Hexacoordinate nitrato complexes were obtained and spectrally characterized at low temperatures using the sublimated layers methodology. For Fe-porphyrins they were obtained via two methods – by NO,[18] THF [19] and NH$_3$[19] interactions with the nitrate complexes of Fe-porphyrins in the sublimed layers,[20] as well as via the nitric oxide dioxygenation reaction (NOD reaction)[21] with oxy globin models. In the case of Co-porphyrins hexacoordinate nitrato complexes were only obtained by the means of NOD reaction. The reason was the impossibility to obtain nitrate complexes in the sublimed layers. Hexacoordinate oxygen complexes with *trans* N-donor ligands (NH$_3$)Fe(Por)(O$_2$) (Por – *meso*-tetraphenyl- and *meso*-tetra-*p*-tolyl-dianions)[21] and (L)Co(Por)(O$_2$) (L - NH$_3$, Py),[22,23] obtained at low temperatures were used as model compounds. Their interaction with NO resulted in formation of the hexacoordinate nitrato complexes that were stable at low temperatures. In all the cases, the formation of hexacoordinate nitrato complexes of Fe-porphyrins was accompanied with the transition of the nitrate ligand from bidentate to monodentate mode of coordination. This change was expressed in the IR spectrum by a shift of the ν(N=O) stretching band to lower frequencies and significant decrease in its intensity. This band in the monodentate-bound complex is the ν_a(NO$_2$) asymmetric stretching of NO$_2$ fragment containing non-coordinated oxygen atoms. The ν_s(NO$_2$) symmetric stretching is close in frequency to ν_a(NO$_2$) of bidentate complex, but with considerably higher intensity. Consequently, the two high-frequency bands in the spectrum of species coordinated in monodentate fashion have wide differences in intensity. This may serve as a diagnostic tool for distinguishing the coordination mode in the nitrate complexes of metaloporphyrins. The third band, representing the ν(MO-N) stretching vibration of the coordinated nitrate group in monodentate complexes has low intensity and is of little use for diagnostic purposes.

Table 1. IR frequencies of absorption bands of nitrato groups in the spectra of 6-coordinate nitrato complexes of Fe- and Co-porphyrins. In parenthesis the frequencies of the complexes with ^{15}N-containing nitrato group are given.

Complex	ν_a(NO$_2$), cm^{-1}	ν_s(NO$_2$) cm^{-1}	ν(O-N), cm^{-1}	References
(-4Py)Co(M4PyTPP)(η^1-ONO$_2$)	1488(1457) (m.)	1267(1246) (s.)	972(959) (w.)	Current work
(-3Py)Co(M3PyTPP) (η^1-ONO$_2$)	1490(1467) (m.)	1267(1245) (s.)	975(962) (w.)	Current work
(NO)(Fe(TPP)(η^1-ONO$_2$)	1505(1472) (m.)	1265(1246) (s.)	969(954) (w.)	[13]
(THF)Fe(TPP)(η^1-ONO$_2$)	1491(1457) (m.)	1280(1258) (s.)	~997(986) (w.)	[14]
(NH$_3$)Fe(TPP)(η^1-ONO$_2$)	1499(1472) (m.)	1268(1249) (s.)	938(925) (w.)	[14,16]
(NH$_3$)Co(TPP)(η^1-ONO$_2$)	1484(1459) (m.)	1270(1248) (s.)	983(970) (w.)	[18]
(Py)Co(TPP)(η^1-ONO$_2$)	1477(1449) (m.)	1270(1247) (s.)	985(979) (w.)	[19]

(m.) – medium, (s.) – strong, (w.) - weak



Scheme 1.

Another possible way of oxidation of the systems under investigation could be associated with the formation of nitro complexes of porphyrins. Indeed, the auto-oxidation of the dissociated NO with oxygen could have led to the formation of NO_2. As it has been shown previously, NO_2 rapidly interacts with the sublimed layers of **I**, resulting in the formation of penta and hexacoordinated nitro complexes.[24] However, IR spectra of nitro complexes of **I** and **II** are noticeably different from those studied in the current work, and such a reaction pathway can be rejected. However, it should be noted that hexacoordinated nitro complexes are still formed in negligible quantities, as evidenced by the weak band imposed on the porphyrin band in the region of 1310 cm^{-1} (see Figures 2 and 5). It is in this region of the spectrum that the intense $\nu_s(NO_2)$ band of hexacoordinated nitro complexes of Co-porphyrins with *trans* electron-donor ligands, are located.

Comparison of the data (summarized in the Table 1) on IR spectra of the known hexacoordinated nitrate complexes with those obtained in the present study in the systems **I** + NO and **II** + NO gives every reason to believe that the structures demonstrated in Scheme 1 are realized in the sublimed layers.

Further evidence on the formation of hexa-, rather than penta-coordinated nitrato complexes is the presence of a high frequency shoulder of the band at 1600 cm^{-1} in the spectrum of the oxidized product of **I** + NO (Figure 5, solid line). It should certainly be related to the vibration of the pyridyl group, located in a *trans* position to the coordinated nitrato group. Cobalt oxidation leads to a stronger bond between the metal and the pyridyl group and to a larger high-frequency shift of this band.

Interaction of the nitric oxide with oxygen complexes of iron-porphyrin models, oxy-myoglobin and oxy-hemoglobin leads to a rapid reaction, resulting in the formation of a nitrate anion and oxidized forms of iron-porphyrins[21] and heme - metmyoglobin and methemoglobin.[25,26] This reaction is called nitric oxide dioxygenation (NOD reaction) which is the main pathway for NO neutralization in the body during its overproduction [27]. At first glance, the reaction of O_2 with nitrosyl myoglobin Mb(NO) is similar to the reaction of NO with Mb(O_2). This reaction was studied in detail in the works of Skibsted *et al.*,[28, 29] owing in part to its importance to the stability of cured meat. As a result of this reaction the same products, metmyoglobin and NO_3^-, are formed, however, the oxygenation of Mb(NO) is much slower and follows a different rate law. The results obtained are in favor of the following mechanism for the reaction: dissociation of NO, subsequent coordination of oxygen with myoglobin and interaction of NO with the coordinated oxygen via the NOD reaction mechanism, which is yet to be finally established for hemoproteins and model iron-porphyrin compounds.[21,27]

It has recently been shown that the oxy-coboglobin models are also able to carry out the NOD reaction.[22,23] Unlike the Fe-analogues, for which the formation of the hexacoordinate nitrate complexes was taking place at 80-100 K without accumulation of intermediates in spectrally detectable quantities,[21] nitrate complexes of Co-porphyrins were formed at much higher temperatures (~ 170 K). In the meanwhile, the spectra of the intermediates were recorded at lower temperatures, thus, shedding light on the mechanism of the reaction. In particular, the formation of a coordinated peroxynitrite complex at the initial stage of the reaction was shown via experiments using isotope-substitute NO and O_2 and calculations of the vibrational frequencies by the density functional theory.[22,23]

We believe that in the case of the systems studied in the current work, the reaction proceeds according to the mechanism proposed for nitrosyl complexes of myoglobin and hemoglobin. It comprises the following steps: dissociation of NO, oxygen coordination and further reaction of NO with the coordinated O_2 via the NOD reaction mechanism. This is supported by both the formation of nitrate complexes, primarily at sites containing hexacoordinate nitrosyl complexes, in which NO is sufficiently labile, and the noticeable increase of the reaction rate with the increase of the oxygen pressure. Further research is required for the precise characteristics of the stages leading to the oxidation of the coordinated nitrosyl ligand.

Conclusion

Sublimed layers of 5-(pyridin-4-yl)-10,15,20-triphenylporphyrinato)cobalt(II) and 5-(pyridin-3-yl)-10,15,20-triphenylporphyrinato)cobalt(II) ({Co(M4PyTPP)} (**I**) and {Co(M3PyTPP)} (**II**), respectively) form coordination oligomers upon standing. Interaction of NO(^{15}NO) gas with these systems results in formation of the penta- and hexacoordinate nitrosyl complexes, the sixth coordination site of which is occupied by the pyridyl group of the adjacent molecule in the layer. The FTIR spectral data demonstrate that the long-term exposure of these systems to O_2 results in oxidation of the nitrosyl complexes with formation of the hexacoordinate nitrato complexes and the reaction proceeds predominantly with the hexacoordinate nitrosyls. The mechanism of the oxidation most likely includes the dissociation of NO from the hexacoordinate complex followed by O_2 trapping of the resulting (-4(3)Py)Co(M4(3)PyTPP) to give (-4(3)Py)Co(M4(3)PyTPP)(O_2), which then reacts rapidly with NO via the nitric oxide dioxygenation reaction.

Acknowledgments. T.S. Kurtikyan would like to thank the State Committee of Science of the Republic of Armenia for the financial support (grant N 13-1D033).

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Received 07.09.2014
Accepted 30.09.2014